Electronic Supplementary Material (ESI) for CrystEngComm.

Supporting information for *Solubility Enhancements through Crystalline Solid Solutions, Non-linear Tammann Diagram and T-X Phase Diagram of Salicylic acid - Benzoic acid*

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Table 1. **DSC summary for SA-BA**

X(BA)	DSC endotherms	Low temperature endotherm					High temperature endotherm				
mol BA/mol SA+BA		T_{inset}	T_{onset}	T_{peak}	T_{offset}	Enthalpy	T_{inset}	T_{onset}	T_{peak}	T_{offset}	Enthalpy
		°C	°C	°C	°C	J/g	°C	°C	°C	°C	J/g
0	One endotherm						154.07 (0.08)	158.64 (0.006)	159.16 (0.09)	160.98 (0.23)	189.56 (4.21)
0.0168	One endotherm						146.383 (1.6)	157.1 (0.4)	158.36 (0.15)	160.64 (0.21)	189.51 (0.28)
0.0265	One endotherm						143.78 (0.81)	156.53 (0.24)	158.01 (0.22)	160.32 (0.248)	185.4 (3.37)
0.0490	One endotherm						137.42 (0.72)	153.61 (0.97)	156.4 (0.42)	158.95 (0.22)	172.01 (2.00)
0.0598	Two separated endotherms	99.95 (3.30)	106.61 (2.81)	110.33 (0.79)	112.00 (0.26)	(0.85) (0.13)	131.69 (1.06)	153.67 (1.15)	156.46 (0.43)	159.19 (0.22)	170.8 (5.86)
0.0682	Two separated endotherms	104.07 (1.74)	109.15 (0.63)	110.94 (0.08)	112.61 (0.24)	1.79 (0.08)	127.52 (1.17)	151.55 (0.43)	155.27 (0.14)	157.85 (0.10)	170.65 (3.89)
0.0899	Two separated endotherms	104.85 (0.23)	109.87 (0.16)	110.91 (0.03)	112.46 (0.12)	4.3 (0.40)	123.04 (1.73)	149.99 (0.19)	154.21 (0.055)	157.66 (0.41)	159.7 (4.46)
0.1014	Two separated endotherms	104.32 (1.05)	110.16 (0.04)	111.02 (0.04)	112.793 (0.09)	6.99 (1.19)	121.54 (2.04)	148.32 (2.12)	153.71 (0.79)	156.58 (1.05)	152.1 (4.99)
0.1228	Two separated endotherms	104.73 (0.39)	110.16 (0.04)	110.96 (0.05)	112.56 (0.19)	9.35 (0.50)	118.14 (2.2)	146.01 (1.58)	152.43 (0.46)	155.79 (0.49)	152.72 (1.98)
0.1634	Two partially overlapping endotherms	103.3 (0.75)	110.2 (0.08)	111.02 (0.005)	112.70 (0.07)	16.48 (0.66)		142.15 (1.460)	150.06 (0.70)	153.39 (0.260	131.36 (8.69)
0.2167	Two partially overlapping endotherms	103.61 (0.83)	110.39 (0.05)	111.23 (0.06)	113.07 (0.17)	23.75 (0.92)		137.52 (0.81)	147.43 (0.17)	150.75 (0.35)	119.31 (3.06)
0.2734	Two partially overlapping endotherms	102.52 (0.67)	110.46 (0.05)	111.25 (0.040	113.17 (0.190	37.46 (3.86)		131.95 (1.79)	142.1 (0.54)	147.24 (1.150)	101.41 (2.84)
0.3090	Two partially overlapping endotherms	103.11 (0.69)	110.37 (0.10)	111.51 (0.08)	113.38 (0.23)	50.07 (0.04)		126.85 (1.61)	139.98 (0.50	144.35 (0.33)	92.798 (1.67)
0.3743	Two partially overlapping endotherms	103.50 (0.33)	110.48 (0.03)	111.65 (0.27)	113.35 (0.26)	64.35 (3.28)		123.39 (1.09)	134.61 (0.62)	140.86 (1.83)	80.03 (1.52)
0.4237	Two partially overlapping endotherms	102.79 (0.77)	110.48 (0.01)	111.68 (0.22)	113.57 (0.23)	81.26 (2.75)		120.39 (0.19)	129.48 (0.21)	136.39 (0.82)	63.45 (2.16)
0.4749	Two mostly overlapping endotherms	102.43 (0.63)	110.97 (0.32)	111.65 (0.14)	113.51 (0.02)	99.39 (3.23)			123.4 (0.15)	132.19 (0.06)	42.52 (1.18)

0.5479	Two mostly overlapping endotherms	102.64 (0.24)	110.92 (0.23)	111.64 (0.14)	114.10 (0.32)	126.61 (1.16)				124.68 (0.71)	15.68 (1.17)
0.5856	One endotherm	102.66 (0.68)	111.40 (0.33)	111.55 (0.09)	116.93 (1.66)	142.29 (2.10)					
0.6632	Two mostly overlapping endotherms	104.87 (0.84)			111.81 (0.11)	78.847 (0.49)		111.58 (0.27)	112.04 (0.19)	115.11 (0.19)	58.4 (0.12)
0.6980	Two mostly overlapping endotherms	103.94 (0.73)	110.98 (0.43)	111.94 (0.32)	111.65 (0.14)	55.23 (2.42)				115.86 (0.03)	81.08 (0.94)
0.7364	Two mostly overlapping endotherms	103.74 (0.75)	110.08 (0.4)	112.48 (0.3)	111.66 (0.32)	43.06 (7.42)				117.09 (1.16)	94.22 (4.8)
0.7730	Two partially overlapping endotherms	104.43 (2.05)		111.44 (0.24)	111.68 (0.24)	17.6 (1.02)		111.86 (0.28)	114.21 (0.31)	118.09 (1.31)	118.97 (5.84)
0.8113	Two partially overlapping endotherms	105.29 (0.12)		111.2 (0.13)	111.74 (0.15)	7.87 (0.73)		113.1 (0.13)	115.45 (0.11)	118.91 (0.18)	128 (3.7)
0.8396	Two partially overlapping endotherms	105.72 (0.14)		111.24 (0.10)	111.83 (0.15)	3.15 (0.10)		114.28 (0.28)	116.21 (0.19)	119.78 (0.36)	131.97 (0.10)
0.8670	Two partially overlapping endotherms	106.875 (0.13)		112.32 (0.13)	112.46 (0.08)	2.09 (0.20)		115.06 (0.33)	117.05 (0.06)	120.22 (0.43)	136.82 (0.89)
0.9053	One endotherm						116.00 (0.63)	117.3 (0.32)	118.52 (0.81)	121.36 (0.76)	138.84 (1.64)
0.9239	One endotherm						116.58 (0.10)	117.9 (0.15)	118.93 (0.21)	121.78 (0.09)	140.38 (0.99)
0.9412	One endotherm						117.99 (0.77)	119.32 (0.83)	120.78 (0.74)	123.43 (0.89)	141.41 (1.21)
0.9652	One endotherm						119.12 (0.22)	120.22 (0.36)	121.41 (0.58)	123.71 (0.35)	142.61 (1.6)
0.9807	One endotherm						120.06 (0.18)	121.53 (0.41)	122.62 (0.36)	123.73 (0.22)	144.71 (1.49)
1	One endotherm						121.2 (0.16)	122.2 (0.08)	123.15 (0.15)	125.22 (0.13)	147.10 (1.20)

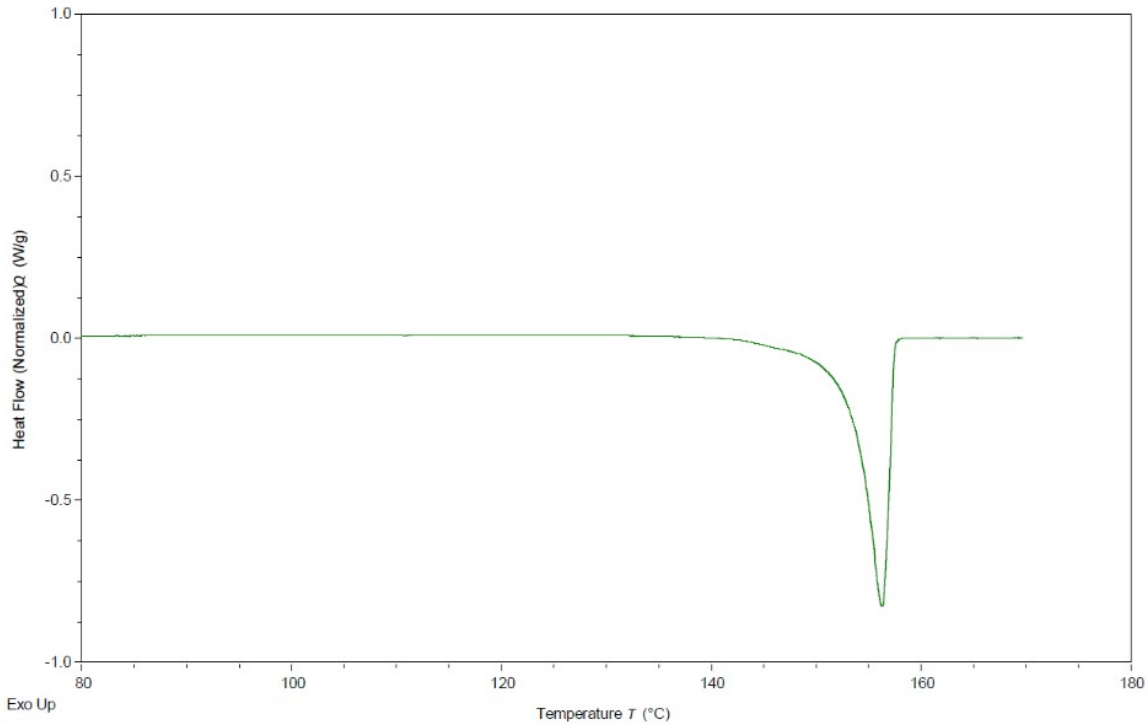

Figure 1. DSC at X(BA) = 0.0490

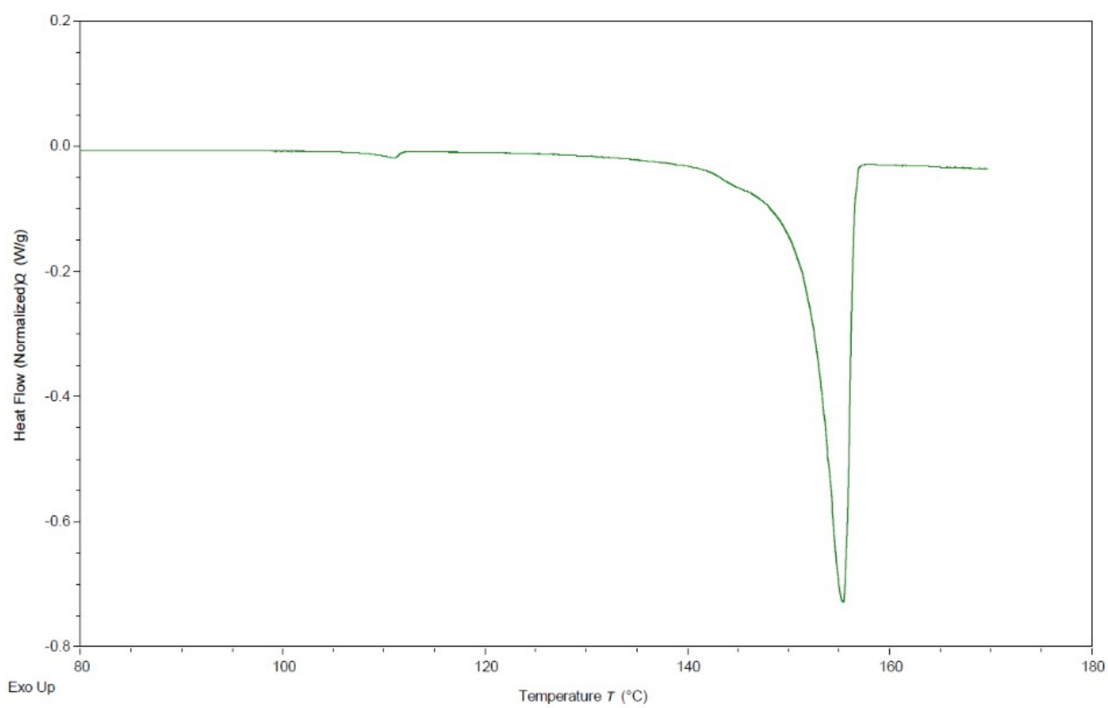

Figure 2. DSC at X(BA) = 0.0682

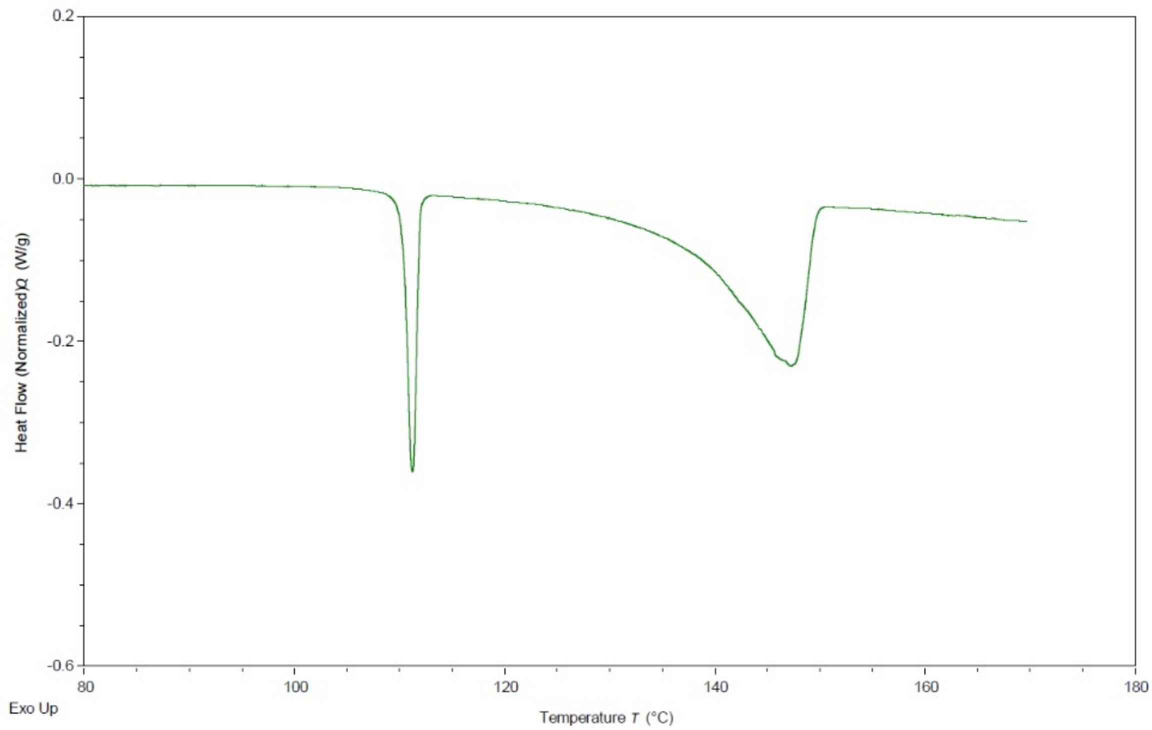

Figure 3. DSC at X(BA) = 0.2167

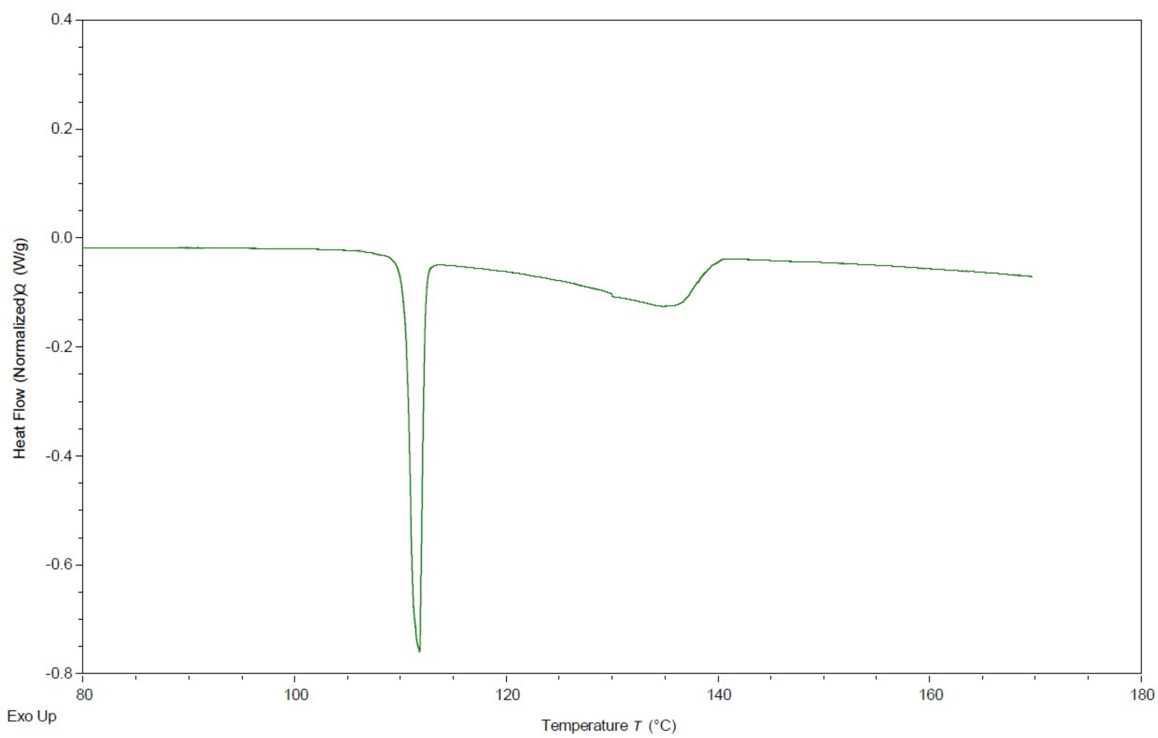

Figure 4. DSC at X(BA) = 0.3743

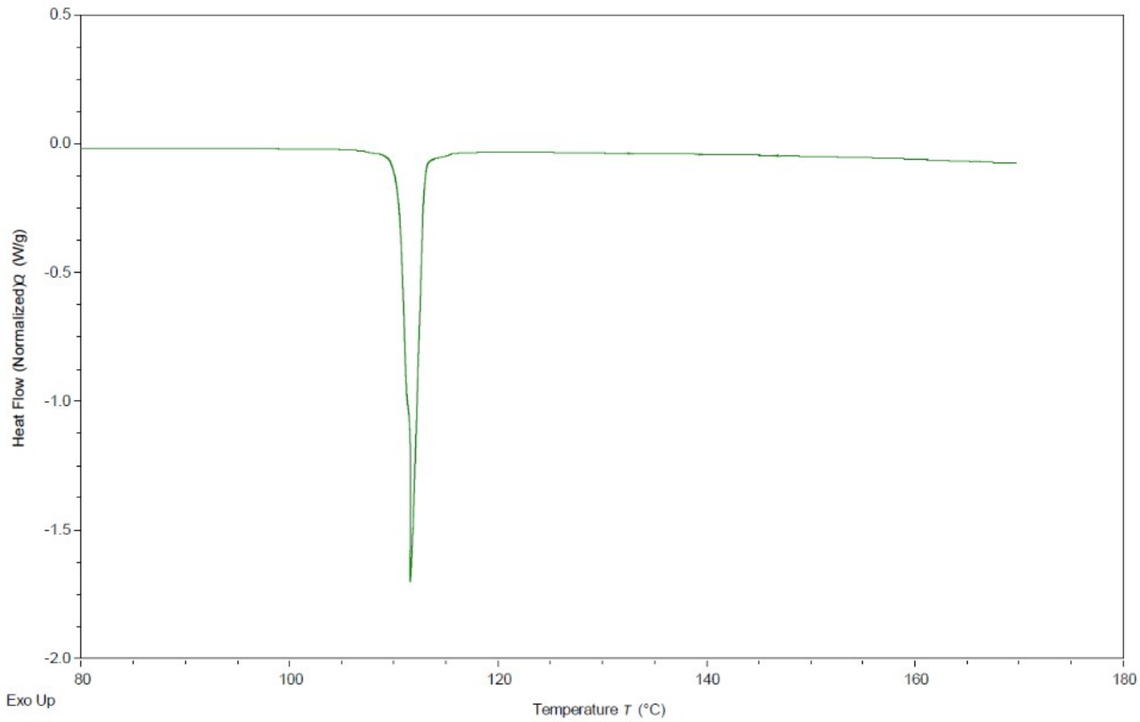

Figure 5. DSC at X(BA) = 0.5856

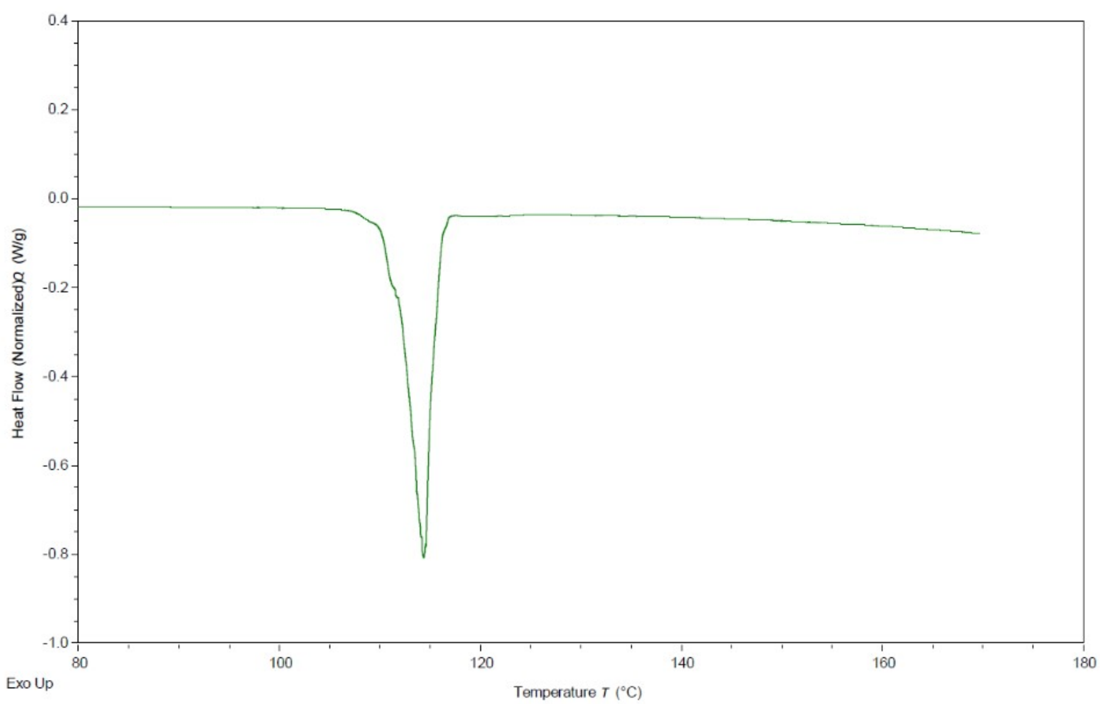

Figure 6. DSC at X(BA) = 0.7730

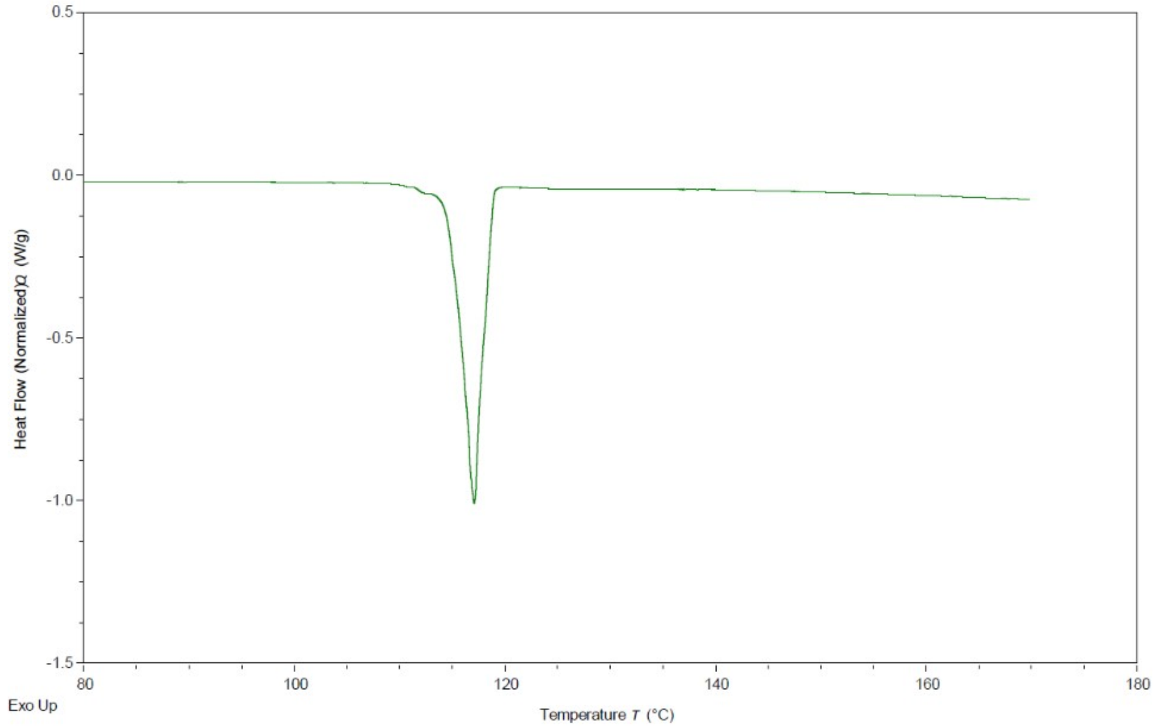

Figure 7. DSC at X(BA) = 0.8670

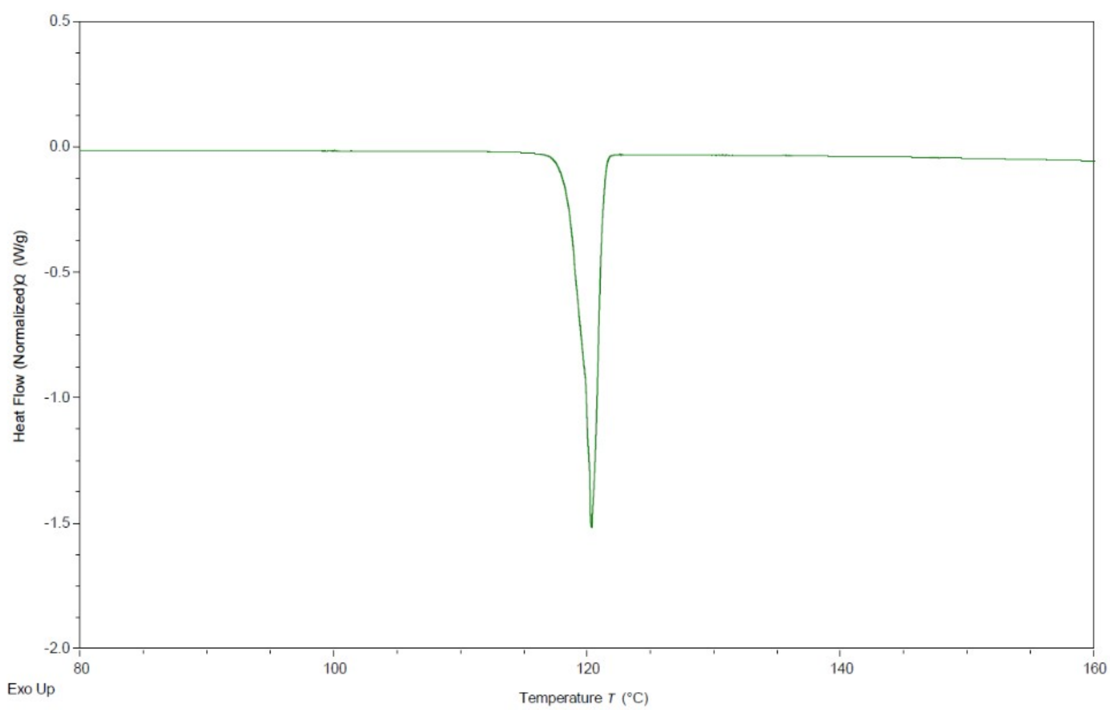

Figure 8. DSC at X(BA) = 0.9412

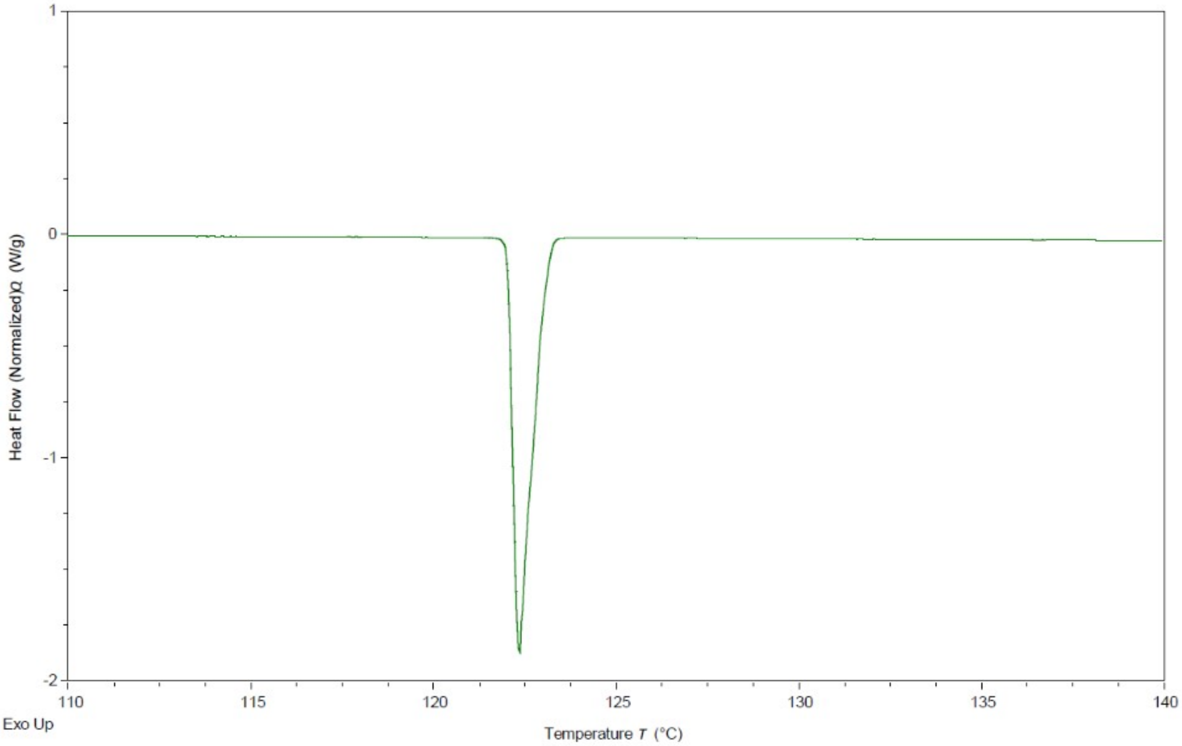

Figure 9. DSC at X(BA) = 1.000

Table 2. Solid-Liquid Equilibria (SLE) summary at 25°C

Solid phase	Liquid	Solid	Liquid	Solid	Conc. of SA	Conc. of BA	X(SA)	X(BA)	X(solvent)
	w% BA in SA	w% BA in SA	mol% BA in SA	mol% BA in SA	mg SA/g solvent	mg BA/g solvent	mmol SA/(mol total)	mmol BA/(mol total)	mol solvent/(mol total)
SA	0%	0%	0%	0%	23.37	0.00	3.6813	0.0000	0.99632
α	3.97%	0.27%	4.47%	0.30%	24.88	1.03	3.9184	0.1834	0.99590
α	5.05%	0.31%	5.67%	0.35%	24.46	1.30	3.8520	0.2315	0.99592
α	10.54%	0.75%	11.75%	0.85%	25.36	2.99	3.9920	0.5318	0.99548
α	11.91%	0.81%	13.26%	0.92%	26.49	3.58	4.1678	0.6372	0.99519
α	17.30%	1.28%	19.13%	1.45%	25.81	5.40	4.0607	0.9609	0.99498
α	16.54%	1.16%	18.32%	1.31%	26.13	5.18	4.1107	0.9217	0.99497
α	17.96%	1.76%	19.84%	1.99%	27.23	5.96	4.2830	1.0602	0.99466
α	26.12%	2.01%	28.56%	2.27%	26.87	9.50	4.2238	1.6889	0.99409
α	23.98%	2.26%	26.30%	2.54%	27.08	8.54	4.2565	1.5188	0.99423
α	31.79%	3.12%	34.52%	3.52%	28.21	13.15	4.4302	2.3358	0.99323
α	35.69%	3.95%	38.56%	4.44%	32.13	17.83	5.0380	3.1625	0.99180
α	34.29%	4.21%	37.11%	4.73%	32.91	17.17	5.1604	3.0456	0.99179
α	44.74%	6.34%	47.80%	7.12%	36.11	29.23	5.6479	5.1714	0.98918
α	46.23%	6.37%	49.30%	7.15%	36.98	31.80	5.7810	5.6221	0.98860
α	46.40%	6.99%	49.48%	7.83%	37.54	32.50	5.8665	5.7447	0.98839
α	47.90%	7.77%	50.98%	8.70%	38.72	35.60	6.0463	6.2880	0.98767
α+β	52.99%	59.05%	56.05%	61.99%	44.02	49.63	6.8517	8.7364	0.98441
α+β	53.64%	9.83%	56.69%	10.97%	42.78	49.50	6.6599	8.7163	0.98462
α+β	53.52%	38.20%	56.57%	41.14%	44.73	51.50	6.9586	9.0625	0.98398
α+β	53.70%	40.29%	56.75%	43.28%	43.65	50.63	6.7931	8.9117	0.98430
α+β	54.36%	74.02%	57.39%	76.31%	42.75	50.92	6.6545	8.9637	0.98438
β	54.89%	83.02%	57.91%	84.69%	41.25	50.19	6.4235	8.8388	0.98474
β	58.97%	85.42%	61.91%	86.88%	33.88	48.70	5.2833	8.5885	0.98613
β	61.18%	86.40%	64.07%	87.79%	31.25	49.25	4.8735	8.6886	0.98644
β	65.94%	89.23%	68.65%	90.35%	24.38	47.21	3.8082	8.3394	0.98785
β	70.25%	91.51%	72.76%	92.42%	19.23	45.40	3.0069	8.0296	0.98896
β	79.22%	93.90%	81.17%	94.57%	11.60	44.23	1.8171	7.8334	0.99035
β	84.05%	96.23%	85.63%	96.65%	8.18	43.09	1.2816	7.6364	0.99108
β	87.15%	96.99%	88.47%	97.33%	6.33	42.90	0.9917	7.6061	0.99140
BA	100%	100%	100%	100%	0.00	42.40	0	7.5256	0.99247

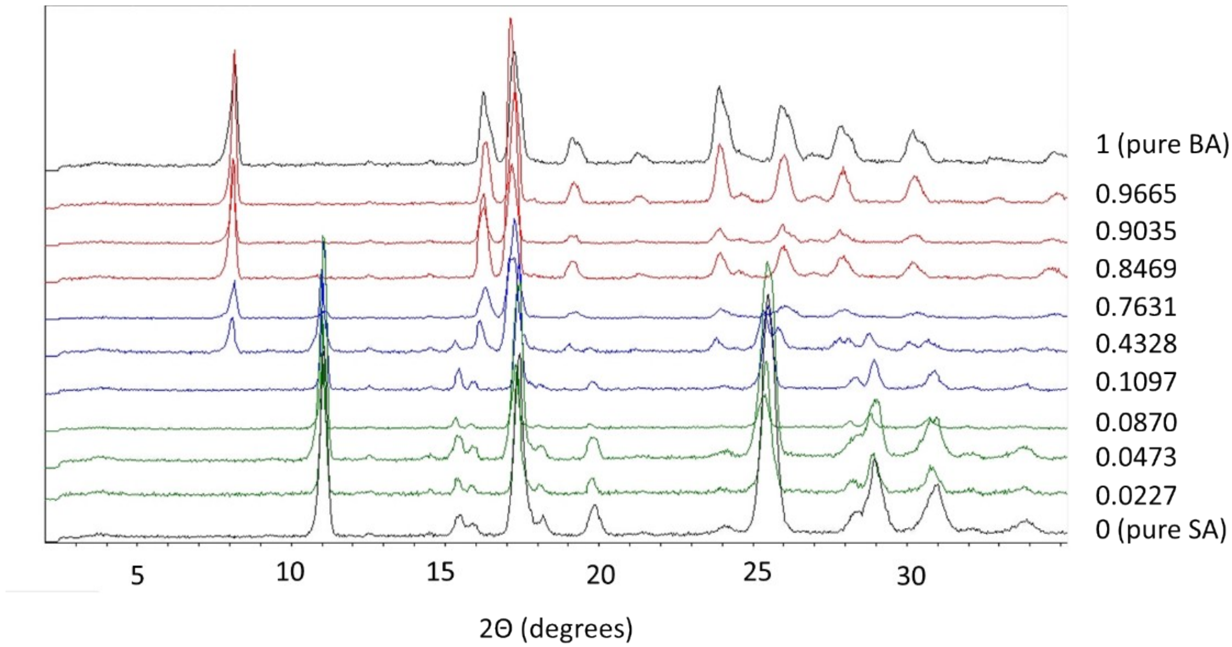

Figure 10. XRPD of solids from SLE study. The compositions are given in mole BA/mol (SA+BA). The color coding represents the solid phases, i.e. green denotes CSS phase α, blue represents CSS α and β, and red corresponds to CSS phase β.

Table 3. Determination of solvi at 25°C through SLE data using three approaches

Solid solution phase	Method[1]	Regression curve	R^2 of regression	Invariant	Solvus mol BA/(mol BA + SA)
α	A	Polynomial	0.9922	0.5669[2]	0.109
α	B	Linear	0.9797	43.58[3]	0.113
α	C	Linear	0.9958	50.43[4]	0.124
β	A	Polynomial	0.9963	0.5669[2]	0.825
Β	B	Linear	0.9726	50.43[4]	0.843
β	C	Linear	0.9981	43.58[3]	0.831

1. Method A: Regression of X(BA) data in solid vs liquid in region a or c to invariant point. Method B: Regression of solubility data of either BA or SA in region a or c to invariant point. Method C: Regression of concentration data of either BA or SA in region a or c to invariant point
2. Units in mol BA/(mol BA+SA)
3. Units in mg SA/g solvent
4. Units in mg BA/g solvent

Methods B: Solubility of α to the invariant point

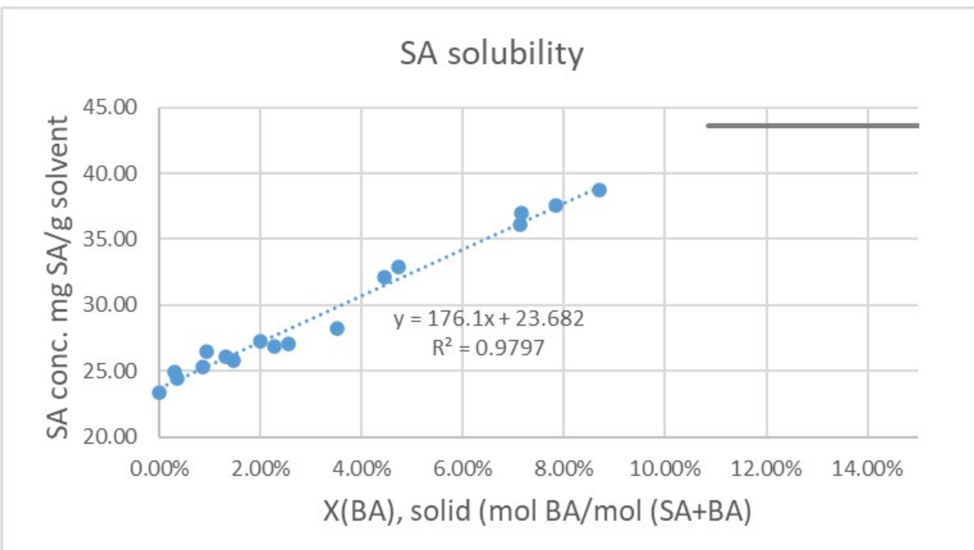

Figure 11. Solubility change of α to invariant point. Linear regression of the solubility increase and extrapolation to the invariant point (method B) yields solvus of α: X(BA) = 0.113

Methods B: Solubility of β to the invariant point

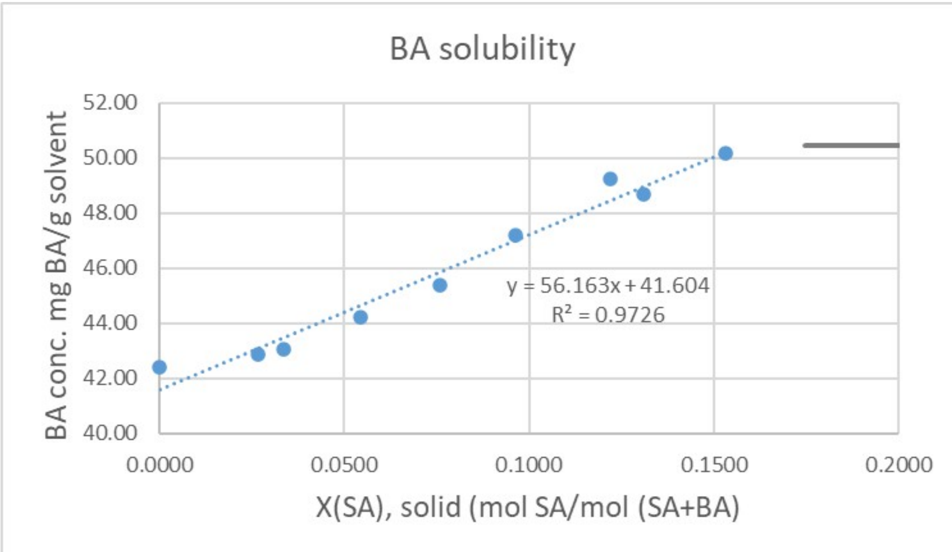

Figure 12. Solubility change of β to invariant point. Linear regression of the solubility increase and extrapolation to the invariant point (method B) yields solvus of β: X(SA) = 0.157 or X(BA) = 0.843

Method C: Concentration of BA to the invariant point

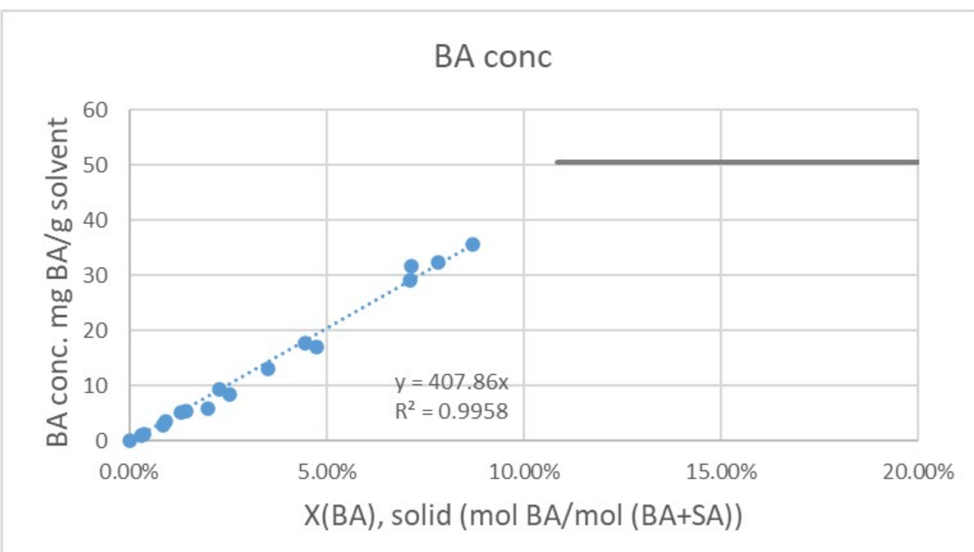

Figure 13. Concentration change of BA to the invariant point. Linear regression and extrapolation to the invariant point (method C) gives solvus for α: X(BA) = 0.124

Method C: Concentration of SA to the invariant point

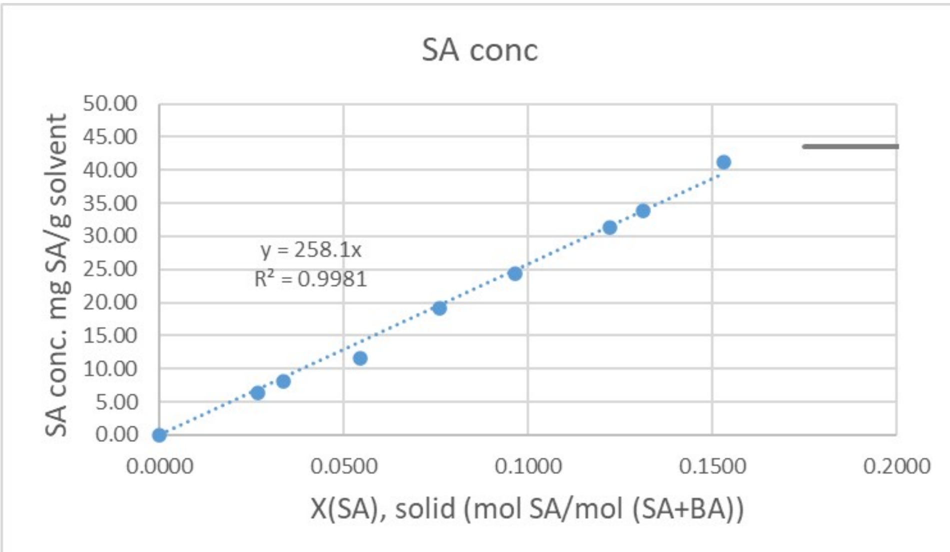

Figure 14. Concentration change of SA to the invariant point. Linear regression and extrapolation to the invariant point (method C) gives solvus of α: X(SA) = 0.169 or X(BA) = 0.831